

Syntheses and Structural Analyses of Cocondensed Resins from Urea and Methylophenols*¹

Bunichiro TOMITA*² and Chung-Yun HSE*³

ユリアとメチロールフェノールからの共縮合樹脂の合成と構造解析*¹

富田文一郎*², チョン・ユン・シー*³

ユリアとメチロールフェノール混合物を酸性下で反応させ、共縮合樹脂を合成する方法を検討した。合成する際の配合モル比や酸性度などの条件を変え生成する共縮合樹脂の構造を ¹³C-NMR と GPC により分析した。共縮合樹脂の結合ホルムアルデヒド量は、フェノール核に対するモル比として規格化された形で表わされ、共縮合樹脂へのユリアの取込み量、縮合度、共縮合の割合や、フェノール核とユリア残基の平均的な置換度が計算された。

その結果、フェノール核がメチレン結合やジメチレンエーテル結合によって自己縮合した構造を部分的に含むものの、共縮合率の高い樹脂を合成できること、さらに、ユリアの水溶液にメチロールフェノールを滴下して合成する改良法においては、共縮合樹脂へのユリアの取込み量が多くなることが判明した。また、メチロール基のユリアとの反応性は、パラ位のものがオルト位のそれより高いこと、反応液の水層には未反応ユリア、無機塩、低分子共縮合物などが存在することが示された。

The reactions of urea with polymethylophenol mixtures in acidic states were investigated by changing the reaction conditions such as the molar ratio and acidity. The cocondensates were analyzed with carbon 13 nuclear magnetic resonance (¹³C-NMR) spectroscopy and gel permeation chromatography (GPC). The quantity of each chemical structure in the cocondensates was normalized and represented to phenolic (P) nuclear as the molar ratio. The ratios of urea (U) incorporated into the cocondensates, the ratios of cocondensation, and the degrees of condensations were determined as were the degrees of substitutions of phenol nuclear and urea residues.

The results were as follows:

- 1) The reactions with the larger molar ratios of U/P were found to decrease self-condensed units effectively.
- 2) A improved method, using the gradual addition of a methylophenol solution to that of urea saved in amount of urea to a great extent in attaining a larger incorporation ratio of urea.
- 3) A greater reactivity was recognized in p-methylol groups than in o-methylol groups for the cocondensations with urea.
- 4) The less the reaction pH, the cocondensations became faster. No significant differences could be observed in the structural compositions by differences of pH between 2.0 and 4.0.
- 5) In the water-soluble parts of the reactants, the large amounts of sodium sulfate and low-molecular-weight cocondensed compounds were recognized as well as unreacted urea.

Keywords: cocondensation, urea, phenol, formaldehyde, ¹³C-NMR.

*¹ Received May 21, 1993.

*² 筑波大学農林工学系 Institute of Agricultural and Forest Engineering, University of Tsukuba, Tsukuba-shi, Ibaraki 305

*³ 米国農務省南部林業試験場 USDA, Forest Service, Southern Forest Experiment Station, Pineville, LA 71360, U.S.A.

be handled adequately even after 3 and 6 h cold-pressing times unlike the boards without IC which needed at least 18 h under compression. In addition, the properties of CBP were improved by the addition of IC resin at all cold-pressing times.

Hot pressing of CBP at 1 h yielded no rigid boards but produced weaker boards at 2, 3, and 6 h hot pressing times. This unfavorable outcome was improved by the addition of IC resin. Furthermore, shortening the hot pressing times to 1 h while simultaneously enhancing the board properties is possible for IC-CBP. Excessive shrinkage of CBP when they were hot-pressed at longer pressing times was eliminated when IC resin was incorporated.

In general, improvement in the dimensional stability (TS and WA) was obtained with both pressing methods when IC resin was added.

SEM observations revealed that the cement hydration which had taken place as indicated by the needle-like cement crystals, was not interfered with the addition of IC resin with both methods of pressing but rather imparted better bonding properties thus resulting in enhancing boards properties.

It is suggested that steam injection pressing technology should be applied to IC-CBP to further shorten the pressing time considering the effects of steam pressure, steam injection time, temperature, and varying of the water content and wood: cement ratio.

Acknowledgements The authors thank the group of Onoda Gement Co., Ltd. for the information supplied regarding cement technology, and Dr. Qian Wang and Mr. Yoshimasa Kishimoto for their suggestions in the conduct of this study.

REFERENCES

- 1) Rowell, R. M.; Spelter, H.; Arola, R. A.; Davis, P.; Friberg, T.; Hemingway, R. W.
- 2) Moslemi, A. A.: *World-Wide Opportunities for Wood Mineral Boards, Wood Based Panels Int.*, 12(2), 7-11 (1992).
- 3) Simatupang, M. H.; Sedding, N.; Habighorst, C.; Geimer, R. L.: "Inorganic Bonded Wood and Fiber Composite Materials", *Forest Prod. Res. Soc.*, 1991, p. 18-27.
- 4) Schmidt, E.: "Fiber and Particleboards Bonded With Inorganic Binders", *Forest Prod. Res. Soc.*, 1989, p. 88-90.
- 5) Evseev, G. A.; Kovalenko, N.: Tr. Arkhangel'sk. Lesotekh, No. 24, 236-9 (1973), [*Chem. Abst.*, 78, 75446 (1973)].
- 6) Moslemi, A. A.: "Fiber and Particleboard Bonded With Inorganic Binders", *Forest Prod. Res. Soc.*, 1989 p. 12-18.
- 7) Galbraith, Jr., C. J.: *Proc. 20th Int. Particleboard/Composite Materials Symp.*, Pullman, 1986, p. 55-81.
- 8) Eusebio, D. A.; Imamura, Y.; Kawai, S.; Sasaki, H.: *Mokuzai Gakkaishi*, 39, 31-39 (1993).
- 9) Lahtinen, P. K.: "Inorganic Bonded Wood and Fiber Composite Materials", *Forest Prod. Res. Soc.*, 1991, p. 32-34.
- 10) Newman, K.: "Concrete Systems (Composite Materials Handbook 8)" 1966, p. 336-452.
- 11) Hachimi, M.; Moslemi, A. A.: *Forest Prod. J.*, 39, 55-58 (1989).
- 12) Lee, A. W. C.; Hong, Z.: *Forest Prod. J.*, 36, 87-90 (1986).
- 13) Wilson, J. B.: Paper presented at the Symposium on Wood Adhesives, Madison, 1980.
- 14) Ahn, W. Y.; Moslemi, A. A.: *Wood Sci.*, 13(2), 77-82 (1980).
- 15) Parameswaran, V. N.; Broker, F. W.; Simatupang, M. H.: *Holzforchung*, 6, 173-178 (1977).

1. INTRODUCTION

In a previous paper in another journal,¹⁾ the reactions of urea with methylphenols under acidic conditions were reported as being investigated using 2- and 4-hydroxybenzyl alcohols and crude 2,4,6-trimethylphenol as model compounds. Several new cocondensed compounds were identified from the reactants with carbon 13 nuclear magnetic resonance (¹³C-NMR) spectroscopy and gel permeation chromatography (GPC). Furthermore, the alternating copolymer, the structure of which is tentatively proposed, has been synthesized by the reaction of urea with crude trimethylphenol. This is the first time that the cocondensation between urea and phenol through formaldehyde has been explained clearly. The fact that the alternating copolymer can be synthesized by a simple method under acidic condition is particularly of significance from the viewpoint of developing practical usages. It also was anticipated that the practical cocondensed resins, which may involve certain amounts of self-condensed units between phenols through the formation of methylene linkage or benzylether linkages, might be obtained from crude mixtures of di- and tri-methylphenols without preparing trimethylphenol.

This paper discusses on the cocondensation method using mixtures of polymethylphenols, which were obtained easily by reacting phenol with formaldehyde in an alkaline state. The purpose of this work, therefore, was focused not only on the determination of an effective method to produce the cocondensations but also on characterizations of the chemical structures of the copolymers.

2. EXPERIMENT

2.1 Syntheses of sodium methylphenates

The method developed by Freeman²⁾ for preparing sodium methylphenates was employed. Sodium hydroxide (106 g, 4 mol) was dissolved in 400 ml of water, and a phenol (418 g of 90% solution, 4 mol) then was added. After cooling to below 20°C, the calculated amount of 37% formalin (for example, 973 g in the case of F/P=3.0; 810 g, F/P=2.5) was added dropwise to the solution with stirring and with cooling by ice. The reaction mixture was allowed to stand at room temperature for at least four days.

Several kinds of methylphenols were synthesized by changing the molar ratio of formaldehyde to phenol (for example, F/P=2.0, 2.25, 2.5, 2.75, and 3.0). After four days, about 0.5 ml of each mixture was diluted with the same amount of D₂O, and its ¹³C-NMR spectrum was taken. Each ¹³C-NMR spectrum indicated the complete consumption of free formaldehyde and the absence of any methylene linkage by the formation of condensation.

2.2 Reactions of urea with methylphenols

The solutions of sodium methylphenates were acidified to pH 5.0 with 50% sulfuric acid. After acidification, methylphenols were liberated, and the solutions became milky. The solutions turned clear again by the additions of calculated amounts of urea. The mixtures were adjusted to the target pHs after adding urea, and were reacted at 90°C. Reaction conditions such as the molar ratio (F/P/U) are cited in the tables and figures. As the reactions proceeded, the mixtures became cloudy. Finally, oily precipitates were separated from the water layers. They were taken and washed with water several times, and dried under vacuums.

The improved method was conducted by using the gradual addition of the methylphenol solution to the solution of urea as followings: urea (12 g, 0.2 mol) was dissolved into 10 ml of water and heated at 90°C after adjusting the pH to 2.0. The solutions of methylphenates (89.4 g, F/P=2.5, phenol 0.2 mol) were acidified to pH 2.0 and dropped gradually into the urea solution with stirring. After the addition was completed in 2 hrs, the reaction was continued under the same conditions for 1 hr. The oily precipitate was treated in a similar way.³⁾

2.3 Gel permeation chromatography

Each dried sample was dissolved into dimethylformamide (DMF) and analyzed by a Liquid Chromatograph ALC/GPC with a R-401 Differential Refractometer (Waters Associates). One Shodex GPC-AD-2002 column (Showa Denko Co., Ltd) was kept at 60°C in a constant temperature bath. The flow rate of DMF was 3.0 ml/min. To measure the content of unreacted urea, about 35 mg of freeze-dried sample of an entire reactant was weighed and dissolved in 2.0 ml of DMF. An aliquot (50 μ l) of the solution was injected after filtration. The amount of unreacted urea was determined by comparing the peak areas

due to urea before and after the reaction.

2.4 ^{13}C -NMR measurements

Each dried sample (300 mg) of the oily precipitate was dissolved into pyridine- d_5 (1 ml) and the solution of sodium methylolphenates was diluted with D_2O . The NMR spectra was obtained with a FT-80A NMR spectrometer (Varian) at a frequency of 20.0 MHz. A 2.0 sec pulse delay time was used with the gated decoupling of protons for quantitative measurements. Chemical shifts were calculated by defining pyridine- d_5 as 123.6 ppm, while internal methanol as 50.0 ppm in a D_2O solution.

3. RESULTS AND DISCUSSION

3.1 Synthesis of Copolymer

The previous paper in another journal,¹⁾ reported that crude 2,4,6-trimethylolphenate purified as a precipitate according to Freeman⁹⁾ was used as a starting material to synthesize the copolymer. The precipitate were dissolved in water and acidified with sulfuric acid before reaction with urea. In the present experiments, the solutions of sodium methylolphenates, which were prepared only by mixing phenol with sodium hydroxide and formalin, were applied directly to react with urea after acidification. It was confirmed from the absence of signals, due to free formaldehyde in the ^{13}C -NMR spectra of the mixtures of sodium methylolphenates, that the methylolations almost were completed after allowing the reaction mixtures to stand at room temperatures for three or four days. Furthermore, the formations of self-condensations between phenols at this stage were absent because the signals attributed to methylene linkages^{3,4)} and benzylether groups,⁹⁾ the chemical shift assignments of which are shown in Table 1, were not observed in the ^{13}C -NMR spectra as shown in Fig. 1. Several kinds of solutions of sodium methylolphenate were employed to cocondense with urea as shown in Table 2, which summarizes the effects of the molar ratio of F/P/U on the structures of the cocondensed resins.

3.2 Structural analyses of cocondensed resins

The emblematic ^{13}C -NMR spectrum of cocondensed resin is shown in Fig. 2. The results of structural assignments and quantitative data are summarized in Tables 1^{1,3-6)} and 2, respectively.

Although the cocondensation between polymeth-

ylolphenol and urea was predominant, the copolymer was indicated to contain self-condensed linkages between phenols to a small extent. This involved the formation of both methylene and benzylether linkages. Three kinds of chemical shifts due to the carbon of methylene linkage, o,o-, o,p-, and p,p-methylene linkages, were determined.^{3,4)} As to the chemical shifts of the carbons due to the benzylether linkage, only the o-linkage has been assigned as 69.7 ppm.⁹⁾ However, the present copolymers showed signals at 72-73 ppm. This down-field shift by 2-3 ppm from the o-benzylether was identical with that observed between the o- and p-methylol groups (61.1 and 64.7 ppm, respectively). Therefore the signals observed at 72-73 ppm were concluded to be attributed to p-benzylether.

As the solutions of polymethylolphenol mixtures of the starting material were confirmed not to contain free formaldehyde, it was shown from ^{13}C -NMR spectra that all of the copolymers did not contain self-

Table 1. ^{13}C -NMR assignments for urea-formaldehyde-phenol resins.

Structures	Chemical shifts (ppm) ^{a)}
Phenolic methylol group	
o-Ph-CH ₂ OH	61.1
p-Ph-CH ₂ OH	64.7
Methylene group between phenols	
o,o-Ph-CH ₂ -Ph	29.6
o,p-Ph-CH ₂ -Ph	35.8
p,p-Ph-CH ₂ -Ph	40.6
Benzylether group between phenols	
o-Ph-CH ₂ -O-CH ₂ -Ph	69.1
p-Ph-CH ₂ -O-CH ₂ -Ph	72~73
Cocondensed methylene group	
o-Ph-CH ₂ -NHCO-	40.6
o-Ph-CH ₂ -N(CH ₂ -)CO-	46.4
p-Ph-CH ₂ -NHCO-	44.2
p-Ph-CH ₂ -N(CH ₂ -)CO-	49.2
Methylene group between ureas	
-NH-CH ₂ -NH-	47.7
-NH-CH ₂ -N(CH ₂ -)-	53.5
-N(CH ₂ -)-CH ₂ -N(CH ₂ -)-	60.0
Phenolic carbon	
HO-C	158~162
Urea residue	
-CO-	162~158

^{a)} The chemical shifts are based on internal pyridine- d_5 as 123.6 ppm.

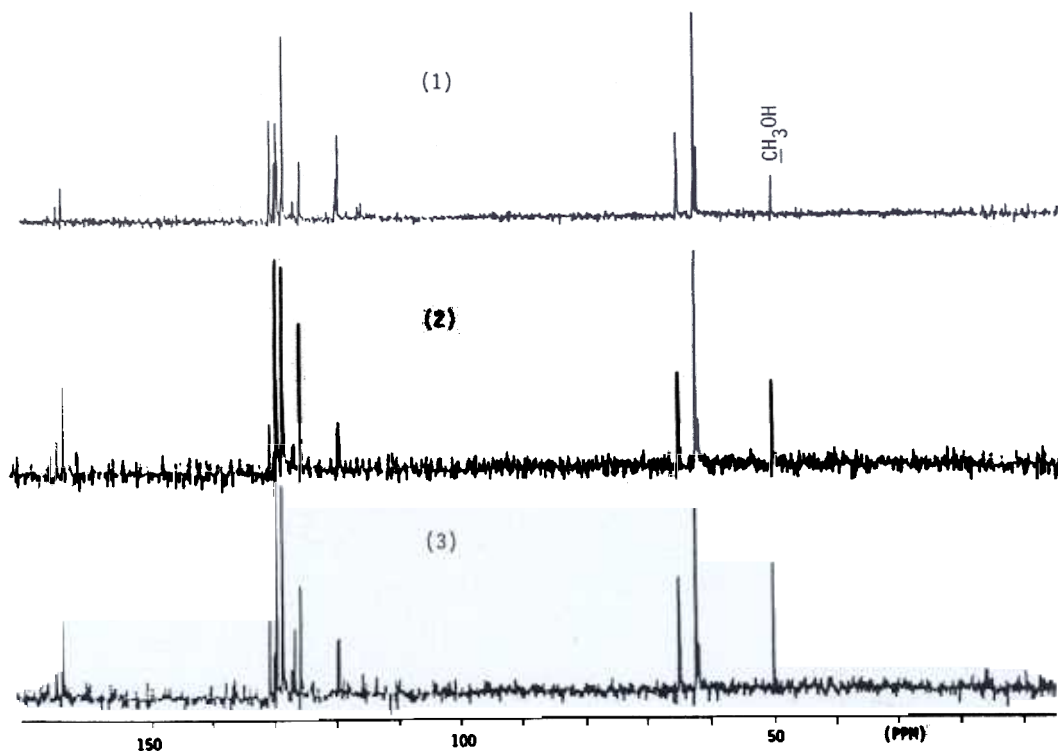


Fig. 1. ^{13}C -NMR spectra of sodium methylolphenates different in the synthetic molar ratio of F/P/NaOH.

Legend: (1): F/P/NaOH=2.2/1/1, (2): F/P/NaOH=2.5/1/1, (3): F/P/NaOH=3.0/1/1.

Note: All spectra were taken after allowed to stand at room temperature for four days after mixing.

condensed units between urea residues⁹ even if the reactions were performed under a strongly acidic condition.

The quantitative measurements of the ^{13}C -NMR spectra were performed with the gated decoupling of protons. The aromatic ring carbons attached to phenolic OH groups appeared in the magnetic field between 152 and 158 ppm in a pyridine- d_5 solution, whereas the carbonyl carbons of urea residues gave signals at 158–162 ppm according to the substitution pattern. Each quantity of combined formaldehyde was normalized and represented as the molar ratio (F/P) against phenolic nuclear by using their integral values in Table 2. The ratio of urea incorporated into the copolymer also was normalized as the molar ratio of U/P.

The normalized concentration of each carbon was determined and represented as follows:

[1]: phenolic methylol group (F/P).

[2]: self-condensed methylene group between phenols (F/P).

[3]: benzylether group (F/P).

[4]: cocondensed methylene group (F/P).

[5]: self-condensed methylene group between urea (F/P).

[6]: total combined formaldehyde (F/P).

[7]: phenol ring (1).

[8]: urea residue (U/P)

The total combined formaldehyde can be obtained by Equation [a]:

$$[6] = [1] + [2] + [3] + [4] + [5] \quad [a]$$

The rate of condensation (R) of the copolymer can be calculated by Equation [b]:

$$R = ([2] + [3]/2 + [4] + [5])/([7] + [8]) \quad [b]$$

Accordingly the degree of polymerization or condensation (P_n) is obtained by Equation [C]:

$$P_n = 1/(1-R) \quad [c]$$

When the copolymer contains the self-condensed

Table 2. ^{13}C -NMR analyses of urea-formaldehyde-phenol resins.¹

Resin Nos.	II	III	IV	V	VI	VII	
Synthetic molar ratios (F/P/U)	2.2/1/1	2.2/1/2	2.5/1/1	2.5/1/2	2.5/1/3	3.0/1/1	3.0/1/3
Reaction pHs	2.25	2.30	2.0	2.3	2.0	2.2	3.0
Reaction times (min) at 90°C	60	60	30	30	30	60	180
[1] Phenolic methylol group	0.71	0.71	0.81	0.73	0.67	1.10	1.12
o-Ph-CH ₂ OH	0.71	0.71	0.81				1.22
p-Ph-CH ₂ OH	—	—	—				—
[2] Methylene group between phenols	0.19	0.27	0.30				0.17
o, o'-PH-CH ₂ -Ph							
o,p-PH-CH ₂ -Ph	0.19	0.27		0.17	0.30	0.21	
p,p-Ph-CH ₂ -Ph	—	—		—	—	—	
[3] Benzylether group between phenols	0.29	0.14		0.20	0.11	0.30	0.14
o-Ph-CH ₂ -O-CH ₂ -Ph	0.29						
p-Ph-CH ₂ -O-CH ₂ -Ph	—						
[4] Cocondensed methylene group	1.05						
o-Ph-CH ₂ -NHCO-	0.29						
o-Ph-CH ₂ -N(CH ₂ -)CO-	0.10						
p-Ph-CH ₂ -NHCO-	0.38						
p-Ph-CH ₂ -N(CH ₂ -)CO-	0.28						
[5] Methylene group between ureas							
-NH-CH ₂ -N							
-NH-CH ₂ -N(CH ₂ -)-							
-N(CH ₂ -)-CH ₂ -N(CH ₂ -)-							
[6] Total formaldehyde ^{b)}	2.24	2.27	2.36	2.42	2.50	2.81	2.9
[7] Phenol (Ph)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
[8] Urea (C=O) (U/P)	0.46	0.69	0.65	0.90	1.0	0.65	1.0
Rates of condensation (R) ^{c)}			0.86	0.84	0.89	0.94	0.86
Degrees of polymerization (Pn) ^{d)}			7.1	6.3	9.1	20	7.1
Rates of cocondensation (Rco) ^{e)}			70%	83%	80%	77%	86%
Degrees of substitution ^{f)}							
Phenols	2.4	2.5	2.7	2.6	2.8	3.0	3.1
Ureas	2.3	1.7	1.5	1.5	1.4	1.8	1.5

^{a)} The quantities of combined formaldehyde and urea are represented by the molar ratio to phenol (F/P) and (U/P). ^{b)} $[6] = [1] + [2] + [3] + [4] + [5]$. ^{c)} $R = ([2] + [3]/2 + [4] + [5])/([7] + [8])$. ^{d)} $Pn = 1/(1 - R)$. ^{e)} $Rco (\%) = 100[4]/([2] + [3]/2 + [4] + [5])$. ^{f)} Degree of substitution, phenol: $([1] + 2[3] + [3] + [4])/[7]$. Urea: $([4] + 2[5])/[8]$.

units between phenolic rings or urea residues, the ratio of cocondensed units (Rco) against all of the condensed units is the important factor in learning its structure. Rco is represented as a percentage by Equation [d] and shows the probability of the occurrence of cocondensation:

$$Rco = 100[4]/([2] + [3]/2 + [4] + [5]) \quad [d]$$

The average degrees of substitutions to one phenolic ring (DS_p) and the urea residue (DS_u) also are important factors, and can be represented as Equations [e] and [f], respectively:

$$DS_p = ([1] + 2[2] + [3] + [4])/[7] \quad [f]$$

$$DS_u = ([4] + [5])/[8] \quad [g]$$

The analytical results of several cocondensed resins

are compared in Table 2. As reported in our previous paper,¹⁾ o-methylol groups of methylolphenols were shown to have less reactivities with urea than with p-methylol groups. Therefore o-methylol groups remained unreacted in fairly large amounts, whereas p-methylol groups were found to be consumed completely. These unreacted o-methylol groups, however, are considered to have potential reactivities either with functional crosslinking agents or curing at high temperatures. As the ratio of cocondensation (Rco) reached 70–86% in each resin, it was concluded that the sequence was composed mainly of the cocondensation. This fact also was supported by the ratios of urea incorporated into these resins.

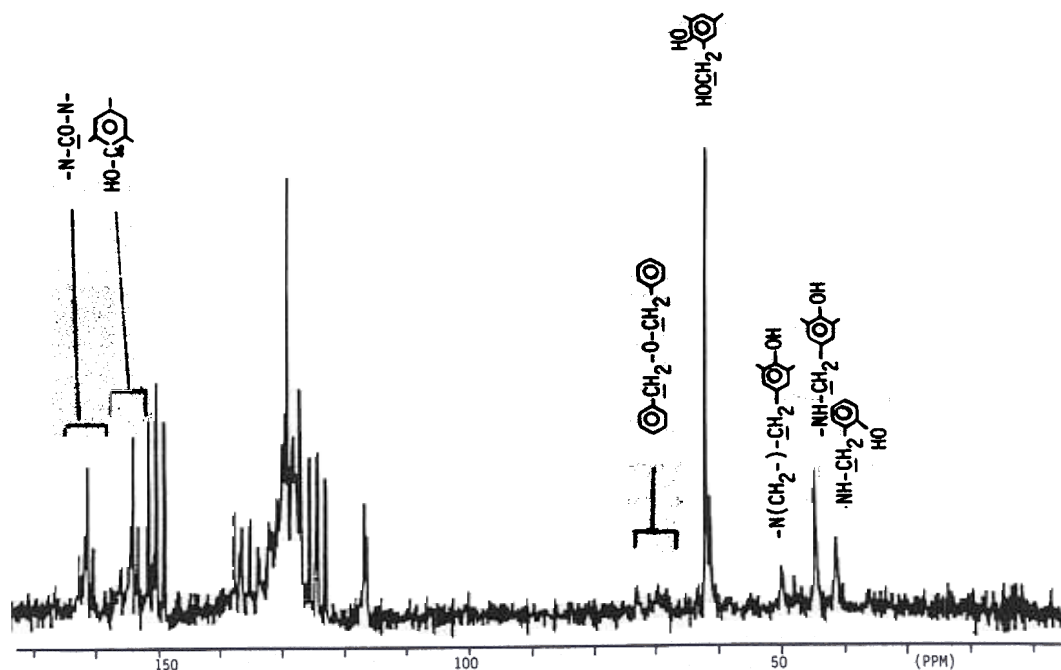
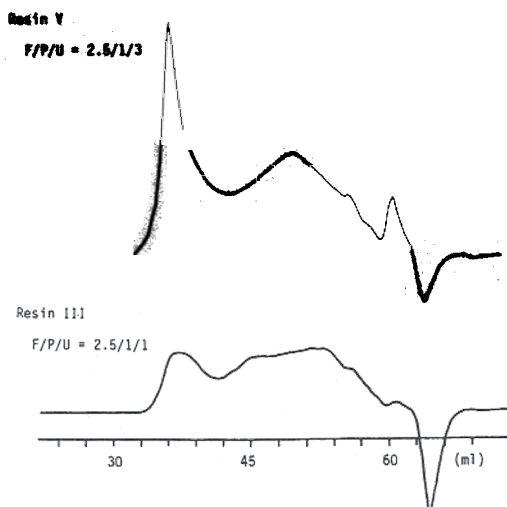


Fig. 2. ^{13}C -NMR spectrum of cocondensed resin from urea and methylolphenols.

Notes: Synthetic conditions: F/P/U=3/1/3, pH 2.0, 85°C, 30 min.



Gel-permeation chromatograms of cocondensed resins of urea and methylolphenols at different molar ratios of F/P/U.

Resins III and V are the same as in Table 2.

3.3 Effects of molar ratios (F/P/U) on cocondensations

Obvious effects on the amount of urea incorporated and the ratio of cocondensation (Rco) could be recog-

nized when the molar ratio of F/P/U was varied. When the same methylolphenol mixture was employed as a starting material, the ratio of cocondensation and the incorporation of urea generally increased as the molar ratio of P/U decreased. For example, the ratio of urea incorporated was 0.65 in Resin III (F/P/U=2.5/1/1), whereas it was 0.90 in Resin IV (F/P/U=2.5/1/2) and 1.0 in Resin V (F/P/U=2.5/1/3). The results also were confirmed by GPC as shown in Fig. 3. It was shown that Resin V contained a large amount of a higher molecular-weight part as compared with Resin III.

On the other hand, increasing the molar ratios of F/P of methylolphenols to the same molar ratio of P/U also was found to enhance significantly the ratio of urea incorporated. For example, it was 0.46 in Resin I (F/P/U=2.2/1/1) and 0.65 in Resin III (F/P/U=2.5/1/1) and Resin VI (F/P/U=3.0/1/1). This result was confirmed further by systematic experiments as shown in Table 3. As the molar ratio of F/P increased, the incorporation ratio of urea increased considerably and it contained a large amount of higher molecular-weight parts, which were confirmed in GPC analyses.

Table 3. The ratios of urea incorporated into resins.

Resin No.	VIII	IX	X	XI	XII ^{a)}	XIII
Synthetic molar ratios (F/P/U) [±]	2.25/1/2	2.5/1/2	2.75/1/2	3.0/1/2	2.5/1/1	
Reaction pHs	2.0	2.0	2.0	2.0	2.0	
Reaction times (min) at 90°	40	40	40	40	180	
Ratios of urea incorporated (U/P)	0.71	0.74	0.83	0.95	0.80	

^{a)} Resin No. XII was synthesized by the gradual addition method.

In the present reaction method, kinetic competition is considered inevitable between the cocondensation and self-condensation of methylolphenols, because strongly acidic conditions were employed. However, both of the self-condensations, the formations of methylene linkages and benzylether linkages, were confirmed to be suppressed by using excessive amounts of urea as shown in Table 2.

From these results it can be concluded that the optimum conditions to attain a desirable cocondensation ratio near P/U=1 is using the methylolphenols synthesized with the molar ratio above F/P=2.5 and the ratio of urea above U/P=2.0. This conclusion was induced from the results of a batch system reaction, where urea was added all at once to the acidified solution of a methylolphenol mixture. On the other hand, the improved method was investigated using a gradual addition of the acidified solution of methylolphenols to the solution of urea. The Resin XII obtained by this method was found to have a considerably larger ratio of urea incorporated (0.80), when compared with Resin III (0.65) having the same molar ratio of F/P/U=2.5/1/1. Although the improved method required a longer reaction time, it decreased the amount of urea to a great extent and attained a greater incorporation ratio of urea.

3.4 Effects of acidity on cocondensation

The effects of acidity on the reaction of urea with a methylolphenol was examined with GPC as shown in Fig. 4. Similar results also were observed in the reaction of urea with p-methylolphenol as reported in the previous paper.¹¹ It is expected that a stronger acidic condition will shorten the reaction time to produce a condensate. Observation in this study indicated that oily products began to separate from water layers within 10–15 min under a pH less than 2.50, whereas it was more than 30 min with a pH of more than 3.0. No significant differences could be recognized with ¹³C-NMR analyses on the structural

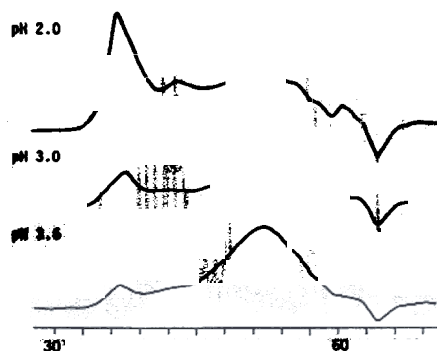


Fig. 4. Gel-permeation chromatograms of cocondensed resins of urea and methylolphenols at different pHs.

Notes: Reaction conditions: F/P/U=2.2/1/1, 90°C, 120 min.

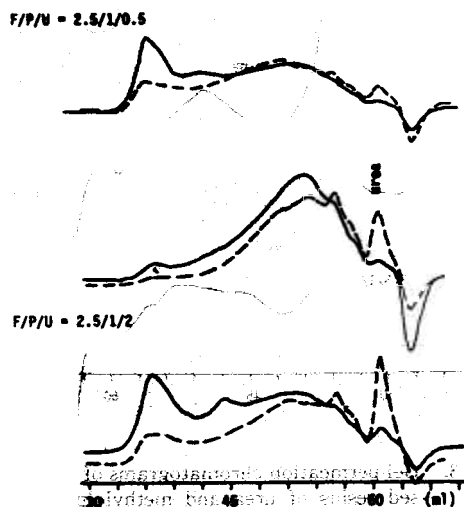


Fig. 5. Gel-permeation chromatograms of reactants of urea and methylolphenols at various molar ratios of F/P/U.

Legend —: Oily precipitate, ----: Whole reactant

Notes Reaction conditions: pH 2.3, 90°C, 60 min.

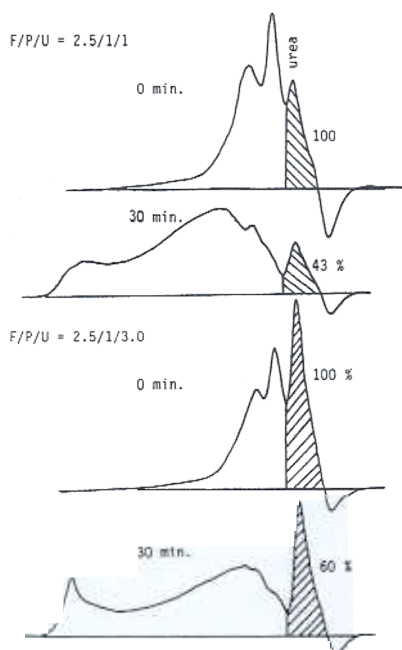


Fig. 6. Quantitative determination of unreacted urea in the reactants of urea and methylphenols with gel-permeation chromatography.

Legend: 0 min: Before starting reaction, 30 min: After reacting for 30 min.

Notes: Reaction conditions: pH 2.0, 90°C.

composition by changing of pH from 2.0 to 4.0.

Although an investigation on chemical kinetics was not performed, it will be emphasized in the development of these cocondensed resins.

3.5 Analyses of water-soluble reactants

Fig. 5 shows the gel permeation chromatograms of the products separated as oily precipitates and the freeze-dried sample of the entire reaction mixture including the water-soluble part. It is noted that the oily products contained greater molecular-weight portions, and that each entire reactant contained a considerable amount of unreacted urea. A simple estimation of the ratio of unreacted urea to the amount of urea-charged initially can be made by GPC data as shown in Fig. 6. In the upper example, the rate of urea incorporated into the resin was estimated to be $U/P=0.57$, because the initial molar ratio of P/U was 1.0, and the rate of reacted urea was 57%. On the other hand, in the bottom example, it was estimated to be $U/P=1.2$, because the initial molar ratio of P/U was $1/3$, and the ratio of reacted urea was

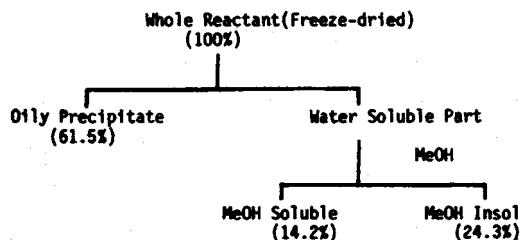


Fig. 7. Fractionation of the reactants of urea and methylphenols.

Notes: Reaction conditions: pH 2.0, 90°C, 120 min.

40%.

The fractionation results of the entire reaction mixture are illustrated in Fig. 7. A fairly large amount of a water-soluble part was recognized. Especially, the methanol-insoluble fraction shared approximately 24% of the entire reaction mixture. This fraction was considered to consist of inorganic salt, sodium sulfate, which was derived from the neutralization of sodium methylphenate with sulfuric acid. Because a large content of inorganic salt is not desirable for practical applications, the synthesis of the methylphenol mixture using smaller amounts of alkaline should be encouraged if the entire reactant involving the cocondensates is intended to be applied directly to practical usages.

The methanol-soluble part extracted from the water-soluble part consisted mainly of unreacted urea, which was confirmed with GPC. It also was confirmed from the ^{13}C -NMR spectra that the methanol extractives contained low-molecular-weight cocondensed compounds and methylenediurea as well as unreacted urea. Methylenediurea was considered to be derived from the reaction of urea with a small amount of free formaldehyde present in the methylphenol solution or dissociated from the methylphenols. The structural determination of low-molecular weight cocondensed compounds, which were water-soluble, was completed as reported in our previous paper.¹¹

4. CONCLUSION

In the previous paper, we succeeded in synthesizing the alternative copolymer from the reaction of urea with trimethylphenol. It is also of significance to find from the present work that the practical cocon-

densated resins, which contain certain amounts of self-condensed linkages between phenols, can be obtained easily by the reaction of a crude polymethylophenol mixture and urea.

Acknowledgement We thank Dr. R. W. Hemingway, USDA Forest Service, Southern Forest Experiment Station, for his advice and encouragement on this research. A part of this work was performed under the Research Agreement No. FP 18-87-076 and FP 19-89-028 between the University of Tokyo and the USDA Forest Service as well as the Grant-in-Aid for Scientific Research (No. 01560176) from Ministry of Education, Science and Culture of Japan.

REFERENCES

- 1) Tomita, B.; Hse, C. Y.: *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 1615-1624 (1992).
- 2) Freeman, J. F.: *J. Am. Chem. Soc.*, **74**, 6257-6266 (1952).
- 3) de Breet, A. J. J.; Dankelman, W.; Huysmans, W. G. B.; de Wit, J.: *Angew. Makromol. Chem.*, **62**, 7-31 (1977).
- 4) Tomita, B.; Matsuzaki, T.: *Ind. Eng. Chem. Prod. Res. Dev.*, **24**, 1-5 (1985).
- 5) Pasch, H.; Goetzky, P.; Grundemann, E. Raubach, H.: *Acta polymerica*, **32**, 14-18 (1981).
- 6) Tomita, B.; Hatono, S.: *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 2509-2525 (1978).